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A new kind of two-dimensional, field-induced phase transition has been discovered in Br_2 graphite intercalation compounds. Similar to, but much more pronounced than Condon domain formation in three-dimensions, it is a Landau level instability which results in two types of domains having different numbers of Landau levels occupied. Study of the dynamics of this phase has revealed a number of domain wall resonances, and strong sensitivity to pinning, with hysteresis observed in some samples. Analysis of the resonance (cont.)

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(Block) 20. ABSTRACT

suggests that the resistivity in the domain phase is considerably lower than in the normal phase -- possible confirmation of a theory that these domains are associated with a type of quantum Hall effect.

In AsF_5-graphite, which displays a field-induced phase transition, x-ray studies reveal a variety of zero-field phase transitions including one which appears to be incommensurate along the c-axis.

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1. Summary of Research Goals and Plans

i) To thoroughly examine the recently discovered Condon phase in Br_2 (and possibly other) intercalation compounds, both to understand the soliton (domain wall) dynamics and to explore the predicted connections between this phase and the quantum Hall effect.

ii) To use magnetooscillations and x-ray diffraction as probes to study superlattice formation in graphite intercalation compounds, particularly in those situations in which magnetic breakdown or field-induced phase transitions suggest that the superlattice may be generated by Fermi surface instabilities.

iii) To search for pressure-induced phase transitions in intercalation compounds, especially via resistivity probes.

2. Status of the Research Effort

a. Condon domains

The majority of our efforts over these six months have been concentrated on the stage 2 Br_2 graphite intercalation compounds, where we have found convincing evidence of strong magnetic interaction[1] with Condon domain formation.[2] Essentially, the oscillations in magnetization M due to the de Haas-van Alphen effect mean that the differential susceptibility $\chi=\partial M/\partial B$ may be large even though M is small. In the Condon domain phase, the sample acts as a perfect differential paramagnet $\partial M/\partial B=1/4\pi$, and the sample is broken up into domains. For a two-dimensional system, the domains correspond to regions where different numbers of Landau levels are filled (e.g., N in one domain, N+1 in the other). This in turn means that the field through the sample is nonuniform, with excess field flowing through regions with fewer Landau levels. This domain phase is closely analogous to the intermediate phase of a type I superconductor, where excess field flows through the sample via normal domains, or to the ferromagnetic domain state. Exploitation of these analogies has greatly aided our understanding of the Condon domain phase.

Condon domain formation has been observed previously in three-dimensional metals.[1] However, in common with all deHaas-van Alphen phenomena, the phase of the oscillations is extremely sensitive to crystalline imperfections--to dislocations or even to mosaic spread in a single crystal -- and the susceptibility of the sample has shown only a smooth variation with field. In sharp contrast, we find that in a two-dimensional system, the transition into or out of the Condon phase is virtually discontinuous: the steps in susceptibility are less than 5G wide, in a field of 6T. That is approximately the homogeneity of the Field across the sample. And this not in a single crystal but in a polycrystalline (HOPG) specimen.

Such an unusual phase is well worth studying in its own right, but Vagner, et al.,[3] have predicted the existence of even stranger effects in connection with such a phase. Within this phase, the Fermi level is effectively pinned between two Landau levels: changing the field changes the relative proportion of the two domains, but within each domain all Landau levels are exactly filled. But this is just the condition of the quantum Hall effect:[4] within each domain, the Hall conductivity is on a particular plateau, and the resistance is zero. Averaging over domains may smooth out the Hall resistivity, but the longitudinal resistance will remain zero except for domain wall resistivity. The search for this effect has guided our intial experiments. A number of obstacles have had to be overcome, but we think we have evidence -- albeit indirect -- for a reduced resistivity.

Our usual inductive probe should have been ideal for these measurements: the out-of-phase a.c. pickup is proportional to the susceptibility, the in-phase component to the resistivity. Unfortunately, we must deal with the domain wall dynamics. In the domain phase, change of magnetization is brought about by changes in the relative proportions of the two domains -- in other words, by motion of the domain walls. Now the walls are pinned, and their motion further damped thanks to induced eddy currents, so the wall behaves as a damped harmonic oscillator. This in turn means that the magnetization cannot exactly follow the applied a.c. field, but lags -- the susceptibility is complex, and its imaginary part feeds into the real (lossy) component of the pick-up, washing out any direct evidence of changes in resistivity. The domain wall dynamics itself is quite interesting, and we have found evidence for at least three resonances,[5] Figs. 1,2. Analyzing the resonance near 720 Hz on the basis of the theory of ferromagnetic domain wall resonance,[6] we find that both the damping and the effective mass of the domain wall vary as B^2. The ratio of these numbers should be proportional to the electrical resistivity, and our measurement suggests that the conductivity is enhanced by ~40x in the domain phase, in accordance with the predictions of Ref. 3. Since ρ_{xx} and σ_{xx} both vanish on a Hall plateau, it is important to understand which conductivity enters the eddy current expression, and we have shown[7] that it is indeed $\bar{\sigma}=1/\rho_{xx}$.

A more direct measurement of ρ would be to put contacts on the sample and directly measure its resistivity. This is non trivial, since the Br_2 rapidly deintercalates when not kept in an atmosphere of excess Br_2, but we have had experience with other intercalation compounds of precooling the sample and attaching pressure contacts, while it is cold. We did this with a Br_2-graphite, and found only an oscillatory resistivity and Hall effect (Fig. 3) with no evidence of sharp steps. We believe that this result is due to pinning effects, and it is in accord with the frequency - dependence of the susceptibility measurements (Fig. 4). At 400 Hz, there appears to be an "unbinding" transition (compare Figs. 1 and 4). Above that frequency the sharp steps in χ are observed; below it the susceptibility becomes a smooth function of magnetic field, with little evidence of domains. We believe that the domains exist below this frequency, but because of pinning, there is a cutoff length in how large excursions they can undergo. Since low frequencies correspond to larger-scale motion, there is effectively a low-frequency cutoff in the resistency (and in χ, which depends on the domain wall dynamics). Such effects are observed in other systems where pinning is important. For instance, in NbS_3 and TaS_3, the charge-density waves[8] are easily pinned, and the high-frequency conductivity is several orders of magnitude larger than at d.c. -- of course we are talking about a very different frequency domain, but the basic effect is the same. We are pursuing direct a.c. resistivity measurements.

Pinning effects are also manifest in a number of other ways: (1) the samples must be cooled initially in a large field, or annealed at high fields for a long time, for the sharp steps in χ to be observed; (2) there is a threshold field, below which only weak oscillations are observed, and this field varies with annealing conditions; and (3) hysteresis is observed in many samples -- χ looks completely different depending on whether the field is swept up or down (Fig. 5).

We are currently undertaking a series of experiments to further understand this unusual phase. We have made a number of different samples. All plates of HOPG starting material show essentially the same susceptibility steps, although with different degrees of hysteresis, but a single crystal and a thick HOPG sample do not show anomalous effects -- again showing sensitivity to local defects. All of our observations have been at 4.2K. Lowering the temperature produced dramatic changes for one hysteretic sample (the steps were smoothed out) but no change for a second sample which had little hysteresis. These changes will be further explored, and we have just built a new probe which will allow study of the oscillations at higher temperatures, as well as simultaneous ac-dc resistivity measurements. We are also planning to measure magnetothermal oscillations and heat capacity, both of which should be very sensitive to the domains.

The clearest proof of the existence of Condon domains was the NMR study by Condon and Walstedt,[9] showing a splitting of the Ag NMR resonance in the domain phase and thereby demonstrating that the magnetic field inside the sample was inhomogeneous. We have tried to duplicate this experiment by looking for Br or C NMR in a high-homogeneity superconducting magnet and dewar owned by R. Meservey at MIT. Unfortunately, while we could observe both resonances in a residue compound, we were unable to observe them in a pristine sample, due presumably to skin-depth problems. The experiments must be done at fields of ~5T, and hence at correspondingly high frequencies. We are presently trying to establish a collaboration with someone who could perform these measurements. There may also be optical absorption anomalies, and we are looking into the possibility of observing them, using C. Perry's high field Raman setup at the Magnet Lab, with Prof. Perry or L. Reinisch (both of NU). Finally, we are trying another observation technique, using fine-line Bi probes to sample the local magnetic field near the graphite surface. This is going to involve a collaboration with IBM for the lithography.

In addition we are trying to develop a better theoretical understanding of the phenomenon. (1) An essential ingredient is understanding the bandwidth of the graphite holes along the c-axis -- how much does the system deviate from two-dimensional. I have developed a model[10] for the c-axis conductivity which allows an answer to this question, and suggests that the bandwidth may be significantly less than the Landau level separation. That is, the intercalation compounds are indeed two-dimensional. (2) The line shape of the susceptibility steps is not the same as predicted by Vagner, et al.[3] This is probably because they neglected the domain wall surface tension, which makes the domains energetically unfavorable over a certain part of the cycle. We are trying to include these effects in the theory. (3) We would like to understand better both the unbinding transition and the high-frequency transition (Fig. 2). This latter may be related to some bulk excitations of the domain (such as helicon waves). (4) The hysteresis suggests there may be nonlinear soliton dynamics in the system, and we would like to understand this better and try to get a real experimental handle on such changes. The fundamental equations seem to be basically the same as those which predict, e.g., chaos in a Josephson junction. (5) At fields above 6T, a second oscillation frequency occurs, due to a larger Fermi surface section. Quinn's group[11] has predicted that in such a case, if the phase of the two oscillations is correct, it is possible to generate a spin-density wave. We should be producing such a state. and would like to know how to distinguish it experimentally. (6) Finally, we are trying to understand whether there is some intimate connection between the two types of quantum Hall effect, or whether the physical similarities are completely accidental.

b. Other Magnetooscillation and X-ray Studies

We are also continuing our study of magnetic breakdown in intercalation compounds. We are also collaborating with Clarke (Michigan) in single crystal studies of HNO_3-graphites, where he does the x-ray analysis and we study the magnetic breakdown. It is interesting to note that in HOPG samples, the super-lattice constant found from magnetic breakdown was $6\sqrt{3}$ times the graphite lattice constant, while Clarke's most recent determination gives $7\sqrt{3}$ for a single crystal sample. The agreement is quite good, and the remaining difference may be real, due to sample differences -- hence the need for our study. Falicov (Berkeley) has recently been calculating the lineshape expected for two-dimensional magnetic breakdown, and we will see if we can test these predictions.

Even more interesting was the field-induced phase transition found in stage 1 AsF_5-graphite with excess F_2. Milliken is trying to make a new sample for magnetooscillation studies, while x-ray studies on another sample show a remarkable series of phase transitions: four transitions between room temperature and 90K and the lowest transition appears to be incommensurate along the c-axis. Such a phase had been predicted in pure graphite to be associated with a charge-density wave,[12] and indeed a field dependent phase transition does occur in pure graphite.[13] However, the charge density distortion is now believed to be in-plane in graphite, and the model of Ref. 12 rested on a band structure effect which should not be present in an intercalation compound. Nevertheless an incommensurate phase suggests a charge-or spin-density wave, such as we originally proposed,[14] and further studies of this phase are underway.

We are also carrying on magnetooscillation investigations of a number of other compounds -- mercurographites, magnetic intercalates -- but so far have not turned up any unusual new phases. Finally, we are looking for Condon domains in other systems, in hopes that the pinning effects might be substantially different. We have seen evidence for it in the HNO_3-graphites and H_2SO_4-graphites, and are undertaking a systematic study of the latter family. Electrochemical intercalation provides precise control over the degree of intercalation, and these compounds are interesting both because of possible Condon domain formation, magnetic breakdown effects, and a commensurate-incommensurate structural phase transition. The magnetic breakdown always occurs in rectangular superlattices, where one dimension is much larger than the other. I believe that such a superlattice forms because of a Fermi surface instability: the short Brillouin zone edge spans the Fermi surface. Hence the incommensurate phase and the breakdown may be related, and this can be tested by varying the charge transfer <u>within</u> a given stage.

c. <u>Pressure Studies</u>

Christos Zahopoulos performed some transport studies in an ungasketed tungsten carbide cell, finding evidence for a phase transition in $FeC\ell_3$-graphite. He suggested numerous improvements of the system-including gasketed measurements -- which another student is beginning to carry out. After finishing his Ph.D., Christos has gone on to a post Doc with W. Paul (Harvard), where he is continuing high pressure studies in a diamond cell. We are hopeful of being able to collaborate with him in future work.

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Figure Captions

Fig. 1. Domain wall resonance in Br_2-graphite: imaginary part of susceptibility (χ_i) vs. frequency showing resonance peaks at 400 and 700 Hz.

Fig. 2. High frequency resonance in Br_2-graphite: χ_i vs field for several frequencies near 12 kHz.

Fig. 3. D.C. resistivity and Hall effect vs. field in Br_2-graphite.

Fig. 4. Real part of susceptibility (χ_r) vs. field for a series of frequencies near the low frequency resonances of Fig. 1. Dashed lines are indicative of "ringing", discussed in Ref. 5.

Fig. 5. Susceptibility vs. field for a different sample of Br_2-graphite. Sweeps with increasing vs. decreasing field show prominent hysteresis.

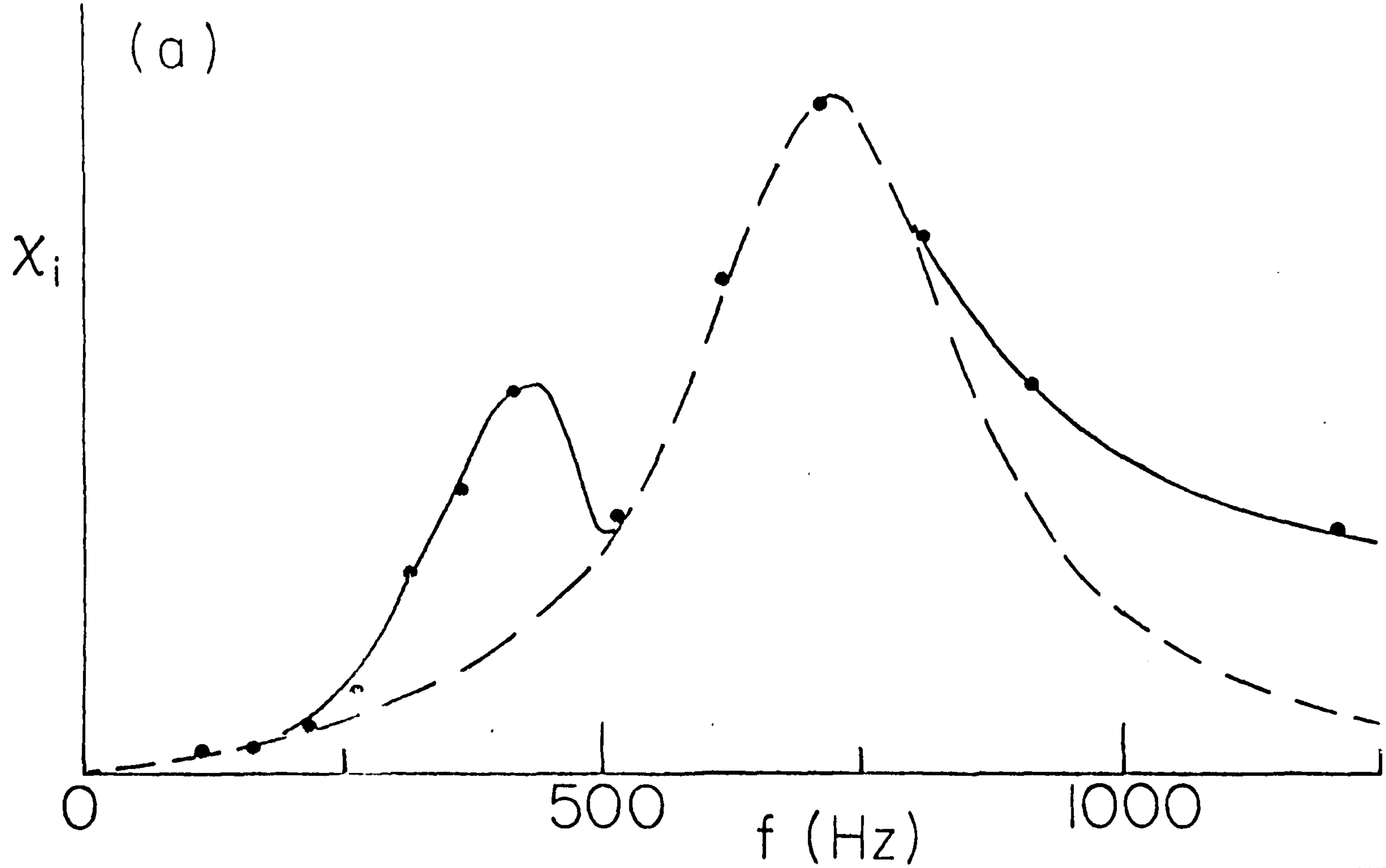

Fig. 1

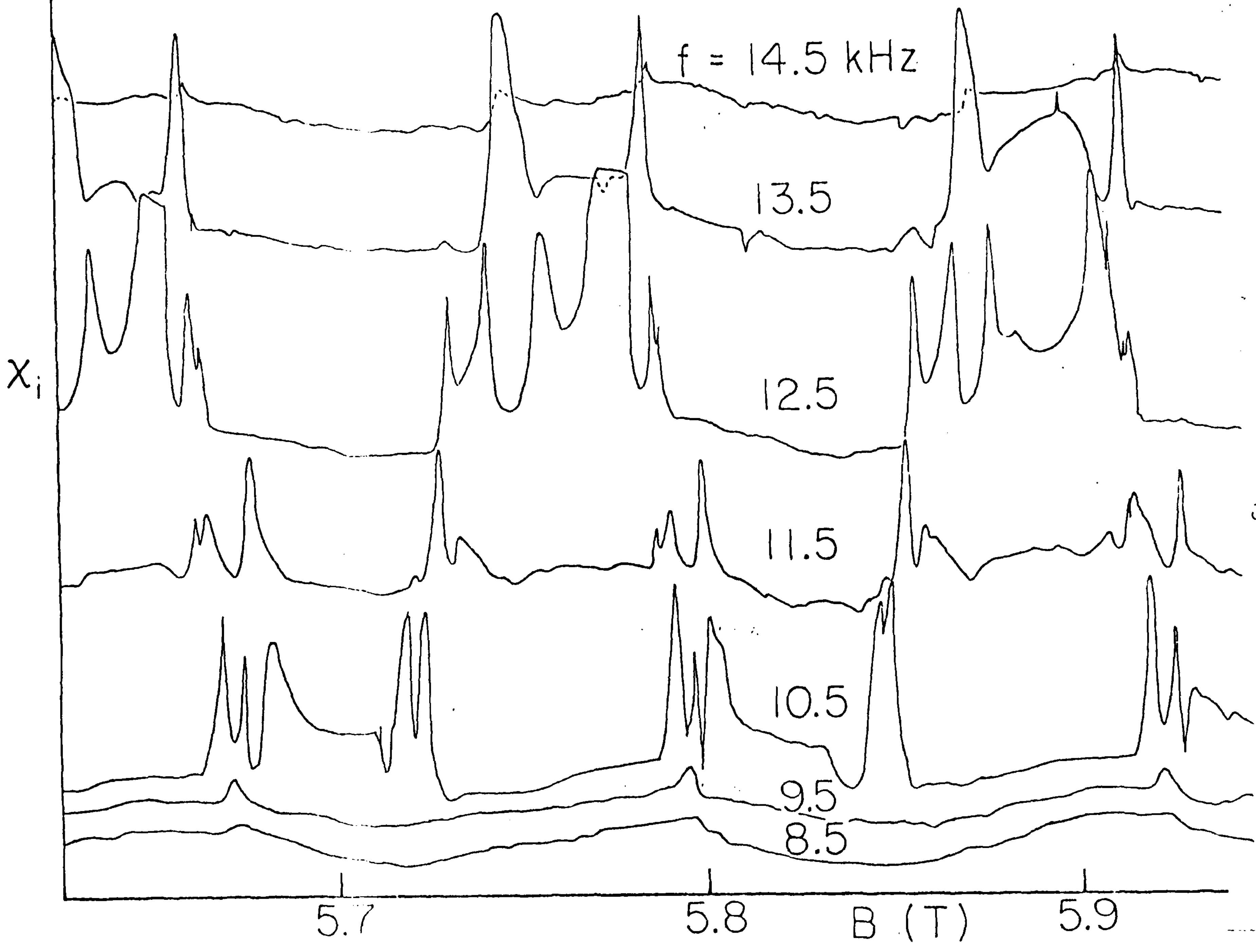

Fig. 2

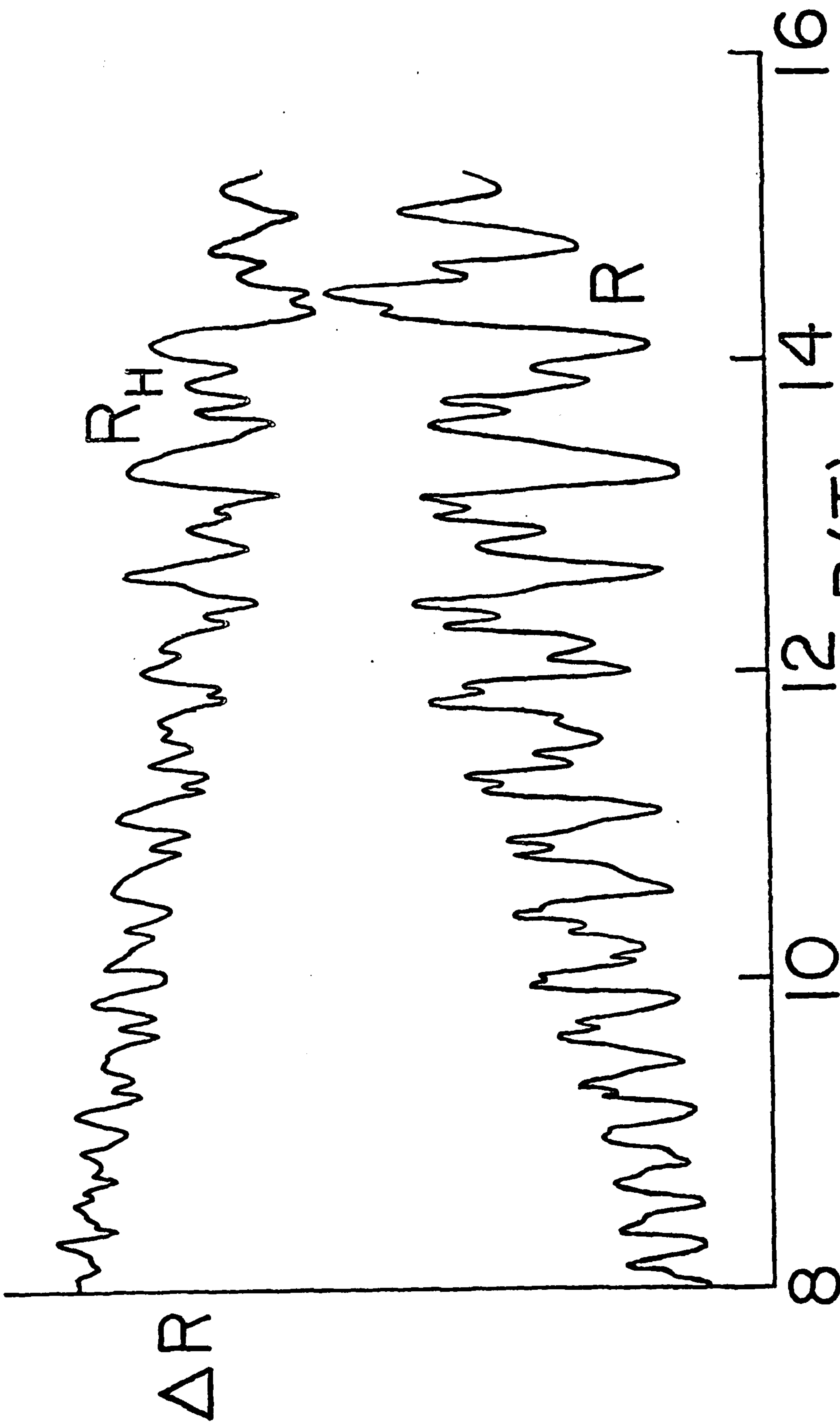

Fig. 3

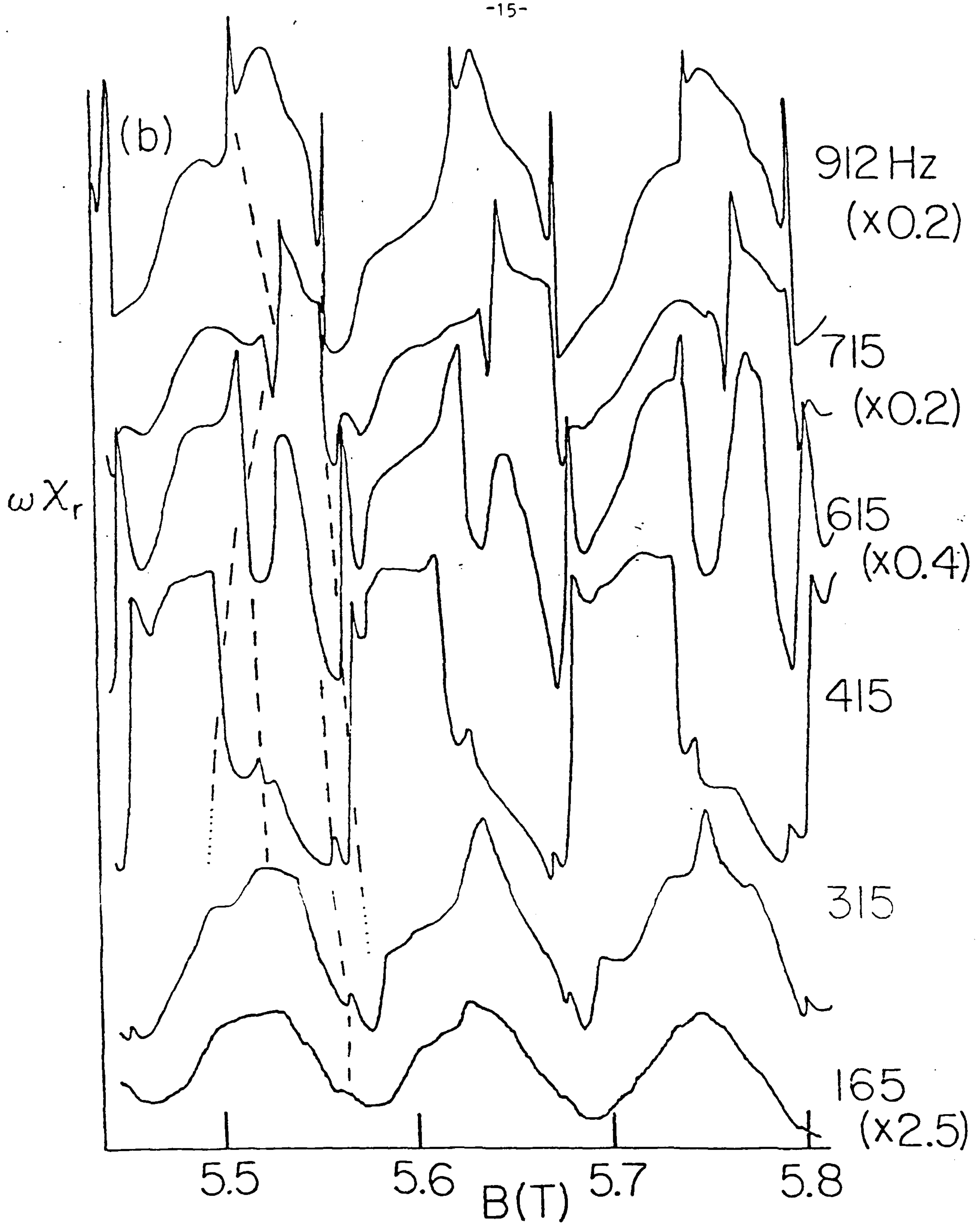

Fig. 4

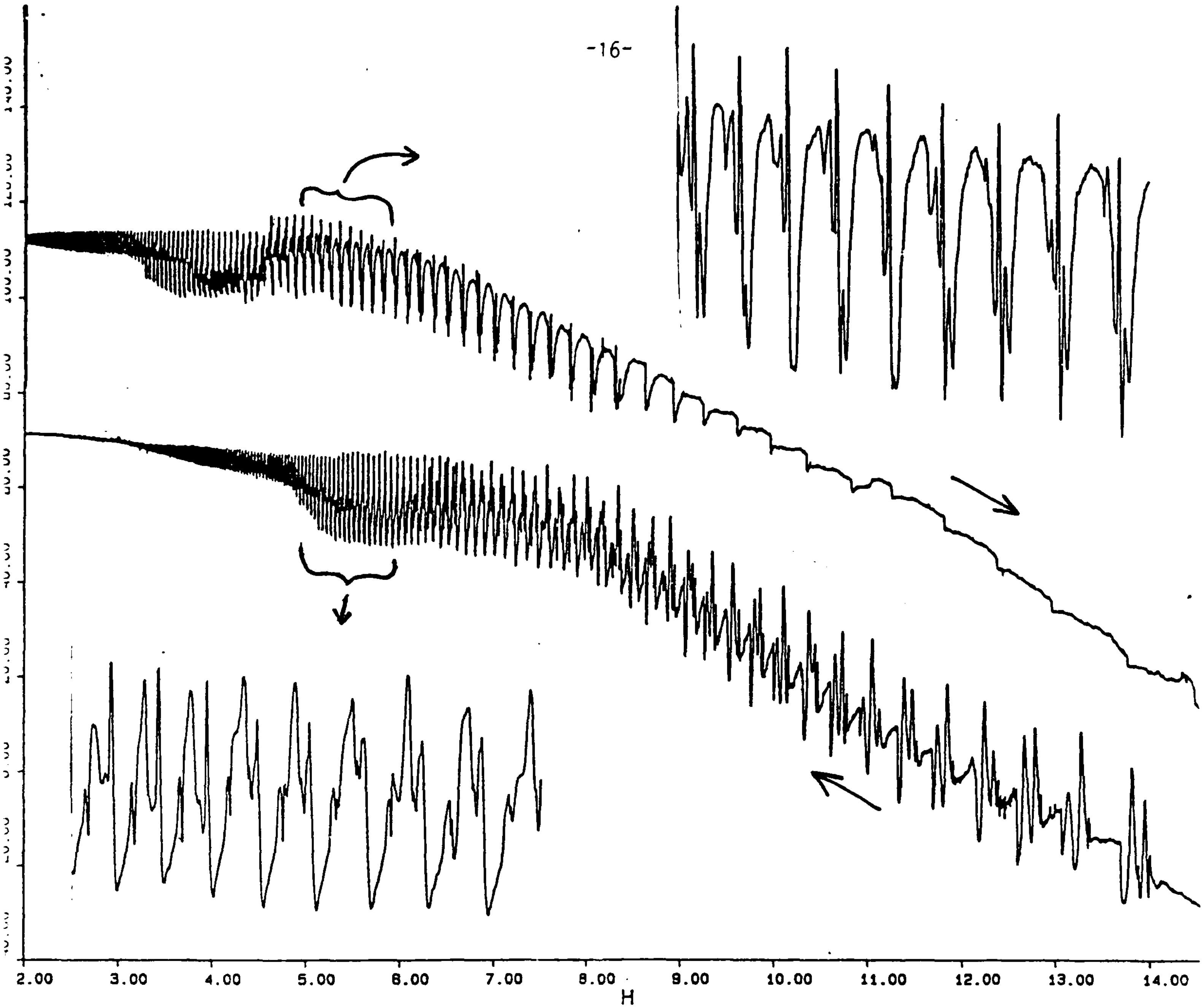

Fig. 5

3. Research Equipment Acquired:

None yet.

4. List of Publications

1. "Field-induced Phase Transition in AsF_5-graphite," R.S. Markiewicz, C. Zahopoulos, D. Chipman, J. Milliken, and J.E. Fischer, to be published, Mat. Res. Soc. Proceedings, 1984.

2. "Magnetic Interference and Breakdown in Intercalated Graphite," C. Zahopoulos and R.S. Markiewicz, ibid.

3. "Magnetooscillations in Intercalated Graphite Single Crystals," M. Meskoob, C. Zahopoulos, and R.S. Markiewicz, ibid.

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7. R.S. Markiewicz and M. Meskoob, "Domain Wall Dynamics in the Condon Phase," in preparation.

8. R.S. Markiewicz, "c-axis Conductivity of Graphite Intercalation Compounds," in preparation.

5. Professional Personnel:

R.S. Markiewicz, Principal Investigator

C. Zahopoulos, Graduate Student†

M. Meskoob, Graduate Student

K. Chen, Graduate Student

B. Maheswaran, Graduate Student

L. Fotiadis, Graduate Student

X. Wu, Graduate Student (Reading Course)

† Received Ph.D. 3/85. Thesis "Fermiology of Acceptor Graphite Intercalation Compounds Using deHaas-vanAlphen and Shubnikov-deHaas Measurements."

6. Interactions

a. Papers presented at scientific meetings:

(i) Refs. 1-3, presented at Materials Research Society Meeting, Boston, Nov. 1984.

(ii) Ref. 6, presented at APS March Meeting, Baltimore, MD, Mar. 1985.

b. Seminars given or arranged:

(i) "Superlattices and Phase Transitions in Graphite Intercalation Compounds," IBM, Yorktown Heights, Oct. 26, 1984.

(ii) "Giant Magnetic Interaction in a Two-Dimensional System: Possible Connection to the Quantum Hall Effect," Northeastern Physics Dept. Colloquium, Nov. 1984.

(iii) "Phase Transitions in Graphite Intercalation Compounds," Chemistry Dept., Northeastern, Feb. 25, 1985.

c. Collaborations

(i) Dr. David Chipman, A.M.M.R.C., Watertown Arsenal: Transmission x-ray studies.

(ii) Prof. J. Fischer, U. Penn., Philadelphia: magnetooscillations in mercurographites.

(iii) Dr. J. Milliken, NRL: magnetooscillations and x-ray studies of AsF_5-graphite with excess F.

(iv) Prof. R. Clarke, U. Mich., Ann Arbor: magnetooscillations and x-ray studies of single crystals of HNO_3-graphites.

(v) Dr. E. Pakulis, IBM, Yorktown Heights: formation of Bi microprobes to observe domains in Br_2-graphite.

(vi) Prof. J. Brooks, B.U., Boston: NMR of Br_2 in Br_2-graphite.

(vii) Prof. L. Falicov, U.C., Berkeley: calculation of magnetic breakdown in 2-d.

(viii) Prof. G. Zimmerman and A. Ibrahim, B.U.: magnetic intercalation compounds ($FeC\ell_3$)

7. Patents

none